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Original Research

Improvement in the protective performance and adhesion of polypyrrole coating on AZ31 Mg alloys

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Abstract

The electrochemical synthesis of polypyrrole (Ppy) coating on AZ31 magnesium alloy was successfully achieved in a solution containing sodium salicylate and monomer of pyrrole through cyclic voltammetry technique. The effect of potential range, passivation pretreatment and number of cycles of polymerization on the quality and protective performance of the coatings was evaluated using surface analysis and electrochemical techniques. Through taking the advantage of charge transfer resistance, current density, corrosion potential, optical microscopy images and SEM micrographs, the optimum condition of synthesis of a Ppy coating with the best adhesion and corrosion protection was determined. The optimal PPy coating synthesized over AZ31 increases the polarization resistance and decreases the corrosion current more than one order of magnitude and shift the corrosion potential about 200 mV toward nobler potentials. The SEM studies showed that Ppy coating have cauliflower morphology of Ppy grains with a diameter ranging from 20 nm to 60 nm.

Keywords: PolyPyrrole; AZ31 Mg; Cyclic voltammetry; Electropolymerization; Corrosion protection

1. Introduction

Magnesium and its alloys are increasingly utilized as structural components in the applications such as aerospace and automotive industry due to their excellent properties like high stiffness/weight ratio, ease of machinability, high damping capacity, castability, weldability and recyclability [1]. However, their high corrosion susceptibility has been a major obstacle to their development in structural applications [2,3]. There are two major reasons for the poor corrosion resistance of magnesium: firstly, the very electronegative potential of Mg makes it very prone to galvanic corrosion, and secondly, the quasi-passive hydroxide film with a formula of $Mg(OH)_2$ is not as stable as other metal oxide films such as aluminum, nickel and chromium oxide, offering better corrosion behavior [4–6].

It is believed that surface treatment or coating can be one of the most cost-effective ways to prevent magnesium alloys from degradation. Moreover, the corrosion protection of a reactive metal such as magnesium through surface treatment or coating is an appropriate approach having no adverse effect on mechanical properties [7,8]. Up to now, several surface modifications such as chemical conversion coatings, anodizing, plating, paint coating, CVD, PVD, plasma spray, thermal spray, sol–gel coatings and electrochemical polymerization have been already suggested to overcome the problem [7–12].

In recent decades, the application of coatings based on conducting polymers such as polyaniline (PANI), polythiophene (PT), polypyrrole (Ppy) on widely used metals has been mostly reported to reduce the corrosion rates [13–15]. Of the conductive polymers, Ppy appeared as a suitable candidate for corrosion protection because of its relatively easy preparation from aqueous solution as well as stability at oxidized state [16]. It is reported that the coatings developed from electrochemical polymerization of pyrrole on active metals such as iron, copper, aluminum and zinc can show good adherence on the surface and proper behavior in the corrosive environments [15–20]. Although Mg and Mg alloys are widely used in

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various industries, few attempts have been reported in the literatures to apply conductive polymer coatings on the metal. The effectiveness of the corrosion protection of an acrylic paint containing electrically conductive polypyrrole for a magnesium alloy has been reported by Troung et al. [7]. In order to improve the corrosion resistance, Jiang et al. [12] electropolymerized pyrrole on a Cu–Ni plated Mg AZ91D. The polypyrrole coating changed the corrosion potential of AZ91 magnesium alloys. Turhan et al. [21] reported the formation of polypyrrole coatings on Mg alloy AZ91D from aqueous solutions of a dicarboxylic organic acid salt by a cyclic voltammetry (CV) method. The polymeric films of Ppy were directly coated onto AZ91D substrates without any pretreatment or intermediate steps. The synthesized coating led to an enhancement in the corrosion resistance of Mg alloy and decreased the degradation rate in 0.1 M Na_2SO_4 solution.

The purpose of this work is to electro-polymerize Py on AZ31 Mg alloy, functioning as an anticorrosion coating with good adhesion to the surface. In this regard, the effect of passivating pretreatment and different coating parameters, namely potential region and number of cycles of the electropolymerization on the coating performance was studied through electrochemical methods and surface analysis. Electrochemical impedance spectroscopy and polarization measurements were employed to investigate the corrosion behavior of the Ppy coated AZ31 Mg alloy in 3.5% NaCl solution.

2. Materials and experimental procedure

2.1. Materials

Die cast AZ31 Mg alloy samples (composition in wt%: Al 3%, Zn 1% with Mg the balance) were abraded with the abrasive papers ranging from 100 to 1200 grit size. The samples were rinsed with distilled water and dried in air, then followed by acetone degreasing. Pyrrole monomer, sodium salicylate and sodium chloride salts were purchased from Merck. All the solutions were prepared using distilled water. Before electrosynthesis, pyrrole was distilled in order to remove any oligomers and oxidized forms and was kept in a dark container at -4 °C.

2.2. Experimental procedure

Electropolymerization of Py on AZ31 Mg alloy was carried out at room temperature in a 0.5 M aqueous sodium salicylate solution containing of 0.25 M Py monomer through cyclic voltammetry technique in different potential ranges (0–1000 mV, 0–1200 mV and 0–500 mV). The cyclic voltammetry was performed at a scanning rate of 20 mV/s for three different cycle numbers (5, 10 and 20). In order to enhance the coating adhesion, a passivation pretreatment was performed on the sample surface. The passivation was carried out using cyclic voltammetry in a swiping potential range of -600 mV to 1200 mV at the rate of 10 mV/s for 2 cycles. The electrochemical synthesis was carried out in a 40 cm^3 glass cell equipped with a conventional three electrode system, including the prepared Mg sample as working electrode, a saturated calomel reference electrode and a stainless steel counter electrode. The exposed area of AZ31 Mg alloy coupons which were used as working electrode was 1.0 cm^2. An EG&G potentiostat/galvanostat model 273 was used for deposition and electrochemical tests.

The adhesion of the polypyrrole films synthesized over AZ31 Mg alloys was assessed according to the ASTM D 3359 standard test method.

The corrosion behavior of the Mg samples covered by Ppy films was examined by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). To perform the electrochemical tests, a three-electrode arrangement with a saturated calomel reference electrode and a platinum counter electrode was used with the specimen (exposed area of 0.12 cm^2) immersed in 3.5% w/w NaCl solution. After 1 h of immersion in the saline solution at ambient temperature, EIS measurements were executed at open circuit potential (OCP) within the frequency domain 100 kHz to 100 mHz using a sine wave of 10 mV amplitude peak to peak. A Solarton 1260 frequency response analyzer (FRA) and Potentiostat–Galvanostat EG&G Model 273A were employed for impedance measurements. All EIS data were analyzed using Zview software. The polarization curves were provided at a scan rate of 1 mV s^{-1} from -250 mV to $+250$ mV of OCP using the same EG&G equipment.

An optical microscope (Gippon model GDCE-30) and a field emission scanning electron microscope (Hitachi FE-SEM SU8040) were used to observe the surface morphology of the Ppy films. It should be noted that all the tests were repeated for three times to ensure the reproducibility of the experiments.

3. Results and discussion

3.1. The electropolymerization potential range

Electropolymerization of Ppy occurs at the potentials which may have negative effect on the Mg alloys so that the Ppy deposition can be prevented by the corrosion of substrate. Therefore, the potential range needs to be chosen appropriately to obtain a high quality coating. To determine the optimum potential range, the electrosynthesis of Ppy on AZ31 Mg alloy was carried out through cyclic voltammetry in a solution containing 0.25 M Py and 0.5 M sodium salicylate in three different potential ranges of 0–1000 mV, 0–1200 mV and 0–1500 mV at a scan rate of 20 mV/s for 10 cycles. It was reported that the vast potential range leads to a decrease in the electrochemical activity and conductivity of polymer films, due to the overoxidation phenomenon. This can result in the coating adhesion reduction and loss of mechanical properties [22,23]. Therefore, the negative potentials were not chosen in this work. Fig. 1 shows the photographs of the surfaces of AZ31 samples which were Ppy coated at the different potential ranges. According to Fig. 1b, a smooth and uniform black Ppy coating was synthesized on the surface in the potential range of 0–1200 mV. A coating with a rainbow appearance formed on

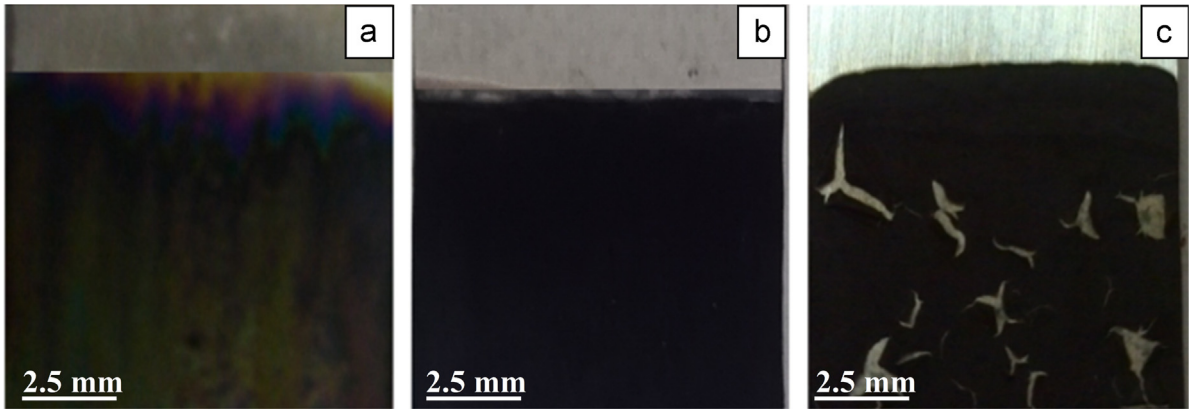

Fig. 1. Photographs of the synthesized coatings in the three different potential ranges (a) 0–1000 mV, (b) 0–1200 mV and 0–1500 mV.

the Mg surface in the potential region of 0–1000 mV, probably due to no sufficient potential to start the Py oxidation.

During the electrosynthesis of Ppy, so many oxygen bubbles covered the electrode surface (Fig. 2), probably due to the decomposition of water into oxygen and hydrogen, according to the reaction Eq. (1) [24]:

$$2H_2O \rightarrow O_2 + 2H_2 \quad (1)$$

Moreover, as the potential became more positive, the reduction of dissolved oxygen might result in the OH^- formation (reaction (2)), increasing the solution pH. In this work, the pH of solutions before polymerization and after first cycle, second cycle and third cycle were 6.5, 7.9, 8.7 and 9.6, respectively.

$$O_2 + 2H_2O + 4e^- \; 4OH^- \quad (2)$$

According to the Pourbaix diagram, an increase in the pH of the aqueous solution decreases the water oxidation potential. As a result, the reaction (1) would occur at lower potential causing severe oxygen gas evolution. Moreover, the OH^- ions may also lead to an overoxidation phenomenon, which is an irreversible reaction of Ppy. The OH^- ions tends to chemically attack to the Ppy chains, resulting in the oxidation of β-C to C=O and formation of carboxyl groups in the Ppy chains. Accordingly, the film may lose its electrochemical activity, due to the damage in conjugated structure. Therefore, the polymer film may encounter a rapid degradation [25,26].

In the case of potentials over 1200 mV, uneven films having low adhesion to the substrate formed, due to the severe oxygen gas evolution as well as coating degradation. Because of the simultaneous formation of oxygen gas and polymer film on the electrode surface, the Ppy might be synthesized on gas bubbles, leading to a rough surface [27]. The failure in the coating formed in the potential range of 0–1500 mV (Fig. 1C) are probably attributed to the exit of gas bubbles. Fig. 3 shows the cyclic voltammograms of AZ31 Mg alloy in a solution containing sodium salicylate and Py monomer for the first three cycles in the optimal potential range. The wide anodic current peak at 1000 mV might be attributed to the potential of magnesium salicylate formation as well as the initiation of Ppy on the electrode surface [28].

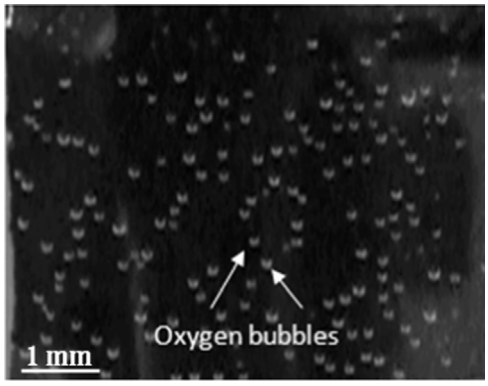

Fig. 2. Photograph of oxygen bubbles formed over the surface during electropolymerization process.

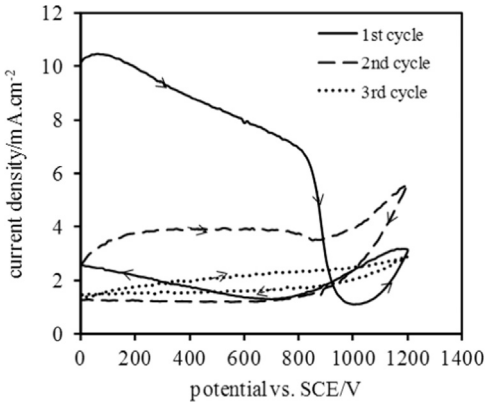

Fig. 3. Cyclic voltammograms of Py electropolymerization for the first three cycles in a solution containing of 0.5 M sodium salicylate and 0.25 M pyrrole.

Studying the Ppy coating on a copper substrate in the presence of salicylate ions, Cascalheira et al. [28] reported the oxidation peak of salicylate at about 1000 mV and described the role of salicylate ions in the formation of passive copper salicylate film. Moreover, the oxidation of Py has been reported at around 900 mV in the literatures [12,29]. With increasing the electropolymerization duration from one cycle to three cycles, the anodic current peak and potential of Ppy nucleation decreased. The reduction in current may be arised from the decrease in magnesium dissolution as a result of Ppy formation. The decline

of nucleation potential is probably connected to the Ppy formation in previous cycles and easier nucleation in the areas.

3.2. Passivation treatment prior to electropolymerization

The adhesion of Ppy coatings synthesized in the optimum potential range was examined in accordance with ASTM D 3359 (Fig. 4). As observed in the Fig. 4, the Ppy film was flaked along the edges and on some parts of the squares. In general, about 30% of the coating was detached from the substrate, indicating the weak adhesion of the electrosynthesized film. In order to enhance the Ppy adhesion and to form a smooth and uniform film on the substrate, a surface passivation treatment was carried out prior to the Ppy electrodeposition. The passivation was performed in a 0.5 M sodium salicylate solution via cyclic voltammetry in a swiping potential of −600 to 1200 mV at a scan rate of 10 mV/s for two cycles.

In the case of potentials higher than 1200 mV and further numbers of cycles, an increase in the substrate passivation may decrease the conductivity of the Mg alloy, having negative effect on the Ppy formation. The cyclic voltammograms of the passivation pretreatment is indicated in Fig. 5. The anodic current peak at a potential about 0 mV might be attributed to a decrease in anodic dissolution of magnesium [21]. Moreover, the formation of magnesium salicylate passive layer could be detected from the anodic peak at about 1000 mV. In the reverse scanning, a corresponding cathodic current peak was observed indicating that the formation of magnesium salicylate is a reversible reaction [28].

Fig. 6 illustrates the voltammograms of Ppy electrodeposition on the passivated AZ31 Mg alloy in 0.5 M sodium salicylate solution containing 0.25 M Py for the first three cycles. Interestingly, the anodic current peak was sharper and lower than that appeared in Fig. 3, probably due to a decrease in the magnesium dissolution through the formation of a magnesium salicylate passive layer on the surface.

The optical microscopy image of the Ppy coatings in the presence and absence of the surface passivation pretreatment is shown in Fig. 7. The passivated surface was thoroughly covered by the Ppy while the grind striations were apparently visible on the surface with no treatment.

The effect of the surface pretreatment on the Ppy coating thickness is indicated in Fig. 8. The cross-sectional optical microscopy images showed that the coating thickness in the absence and presence of surface passivation was about 25.3 μm and 35.1 μm, respectively. In addition to developing a thicker Ppy coating, the passivation of the Mg surface resulted in the formation of a smooth and unifom film, probably due to a decrease in magnesium dissolution as a result of the deposition of magnesium salicylate on the substrate surface.

The role of the surface pretreatment in promoting the adhesion of Ppy coatings was studied through measuring the detachment of the film from a cross-scratch of samples (Fig. 9).

In the case of the surface passivation, some small coating flakes were detached at the intersections of the cuts. In accordance with the ASTM D 3359 standard test method, since less than 5% of the area was affected, the coating adhesion was rated 4B. However, the Ppy coating on the Mg surface with no pretreatment was flaked along the edges and on parts of the squares. The adhesion of the Ppy coating with 15–35% detachment was rated 2B. The significant effect of the passivating pretreatment on the coating adhesion might be

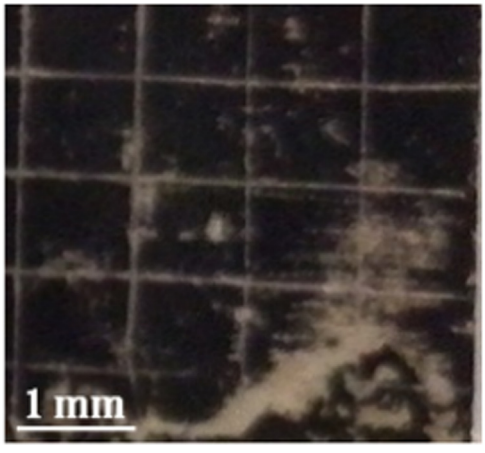

Fig. 4. Result of adhesion test of Ppy coating synthesized in the potential range of 0–1200 mV.

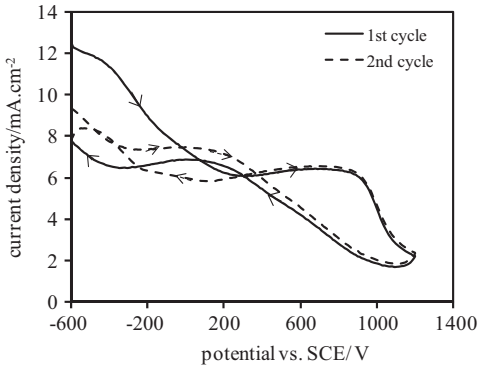

Fig. 5. Cyclic voltammograms of Mg passivation in 0.5 M sodium salicylate solution.

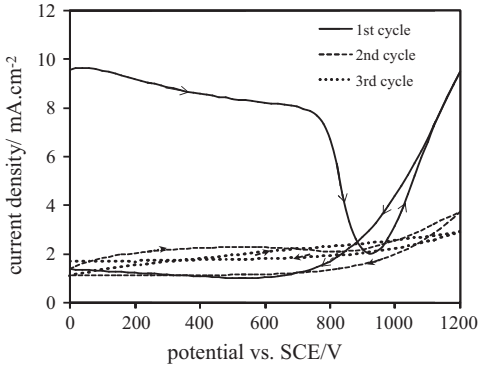

Fig. 6. Cyclic voltammograms of PPy electropolymerization for the first three cycles after passivation treatment in 0.5 M sodium salicylate solution.

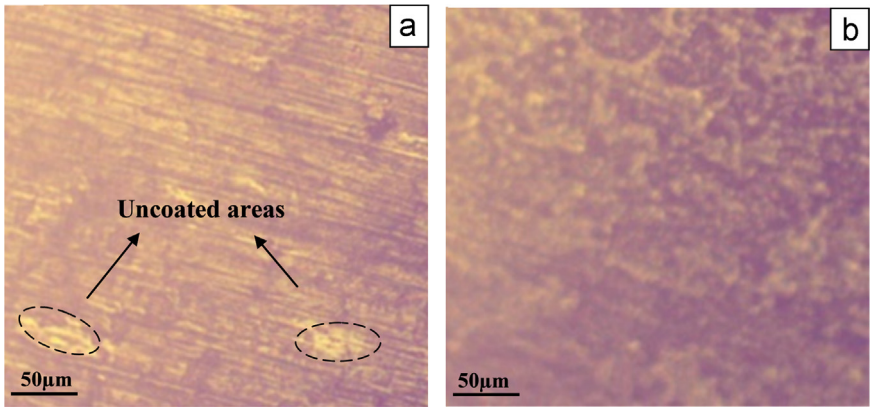

Fig. 7. Optical microscopy images of Ppy coated surfaces (a) without and (b) after passivation in 0.5 M sodium salicylate.

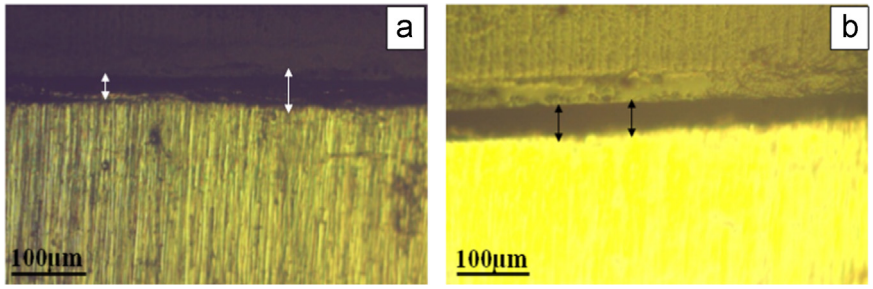

Fig. 8. Cross sectional OM images of Ppy coatings (a) without and (b) after passivation treatment in 0.5 M sodium salicylate.

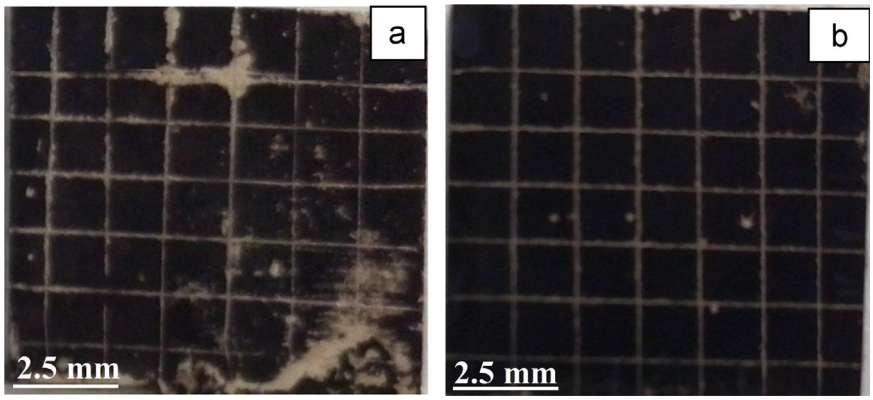

Fig. 9. Results of adhesion test of Ppy coatings (a) without and (b) with passivation treatment.

connected to the formation of a stable magnesium salicylate passive layer, which decreases the magnesium dissolution.

The influence of the surface passivation on the AC impedance spectra and potentiodynamic polarization curves of the Ppy coated AZ31 is indicated in Figs. 10 and 11, respectively. According to the figures, the passivation pretreatment could enhance the charge transfer resistance from 4000 to 5200 $\Omega\ cm^2$, decrease the corrosion current density from 1.3 to 0.25 $\mu A\ cm^{-2}$, and cause a shift in the corrosion potential from -1.5 to -1.36 V.

In the presence of the surface pretreatment, the enhancement in corrosion resistance of AZ31 might be attributed to the better adhesion of the synthesized Ppy coating to the surface which was confirmed previously.

3.3. Cycle number effect on Ppy coating quality

Fig. 12 presents the OM images of Ppy Coatings electrosynthesized for different cycles of 5, 10 and 20. According to Fig. 5 cycle process was not able to cover the surface entirely and the tracks of the abrasive paper were apparent. Electrodeposition for 10 cycles results in the entire coverage of the surface (Fig. 12b). The Ppy coating quality was adversely affected with increasing the electropolymerization cycle over 10.

The 20-cycle Ppy deposition was a time consuming process, leading to the formation of so many bubbles on the surface (Fig. 12c). Furthermore, an increase in the pH of the electropolymerization solution resulted in an overoxidation phenomenon.

The Nyquist plots of the coatings electrosynthesized for different cycles are demonstrated in Fig. 13. An increase in the cycle number from 5 to 10 improved the charge transfer resistance from 1750 to 5200 Ω cm^2. The inferior behavior of the Ppy coating synthesized for 5 cycles might be attributed to the film thickness insufficient for barrier function. On the other hand, it was observed that the increase of cycle number from 10 to 20 leads to a decrease in the charge transfer resistance from 5200 to 1600 Ω cm^2, probably due to an increase in the pH value of the solution at higher cycles. The oxygen gas evolution is intensified at higher pH, which can lead to the formation of a porous coating on the substrate surface. At high OH^- ions concentration, the overoxidation of Ppy films might reduce the film conductivity, and also loosen the adhesion bonds between the metallic substrate and the coating [30,31].

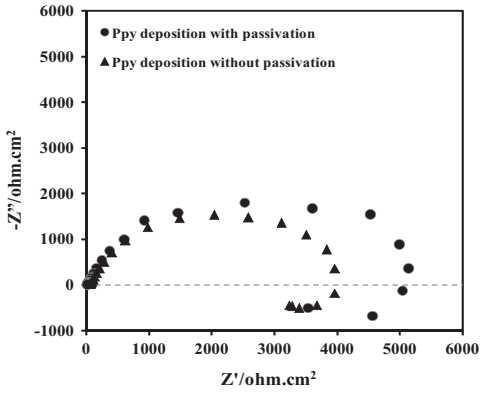

Fig. 10. Nyquist plots of Ppy coated AZ31 Mg alloys coated with and without passivation.

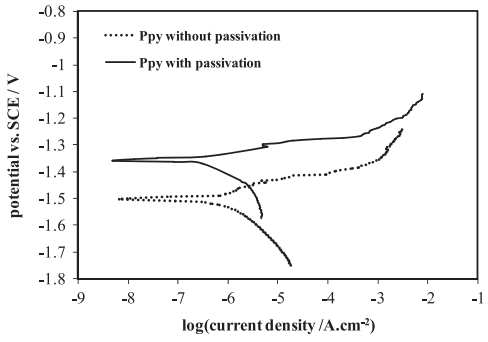

Fig. 11. Potentiodynamic polarization curves of Ppy coated AZ31 Mg alloys coated with and without passivation.

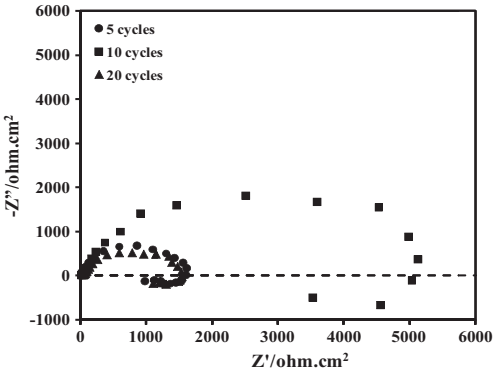

Fig. 13. Nyquist plots of Ppy coated AZ31 Mg alloys synthesized for different cycle number.

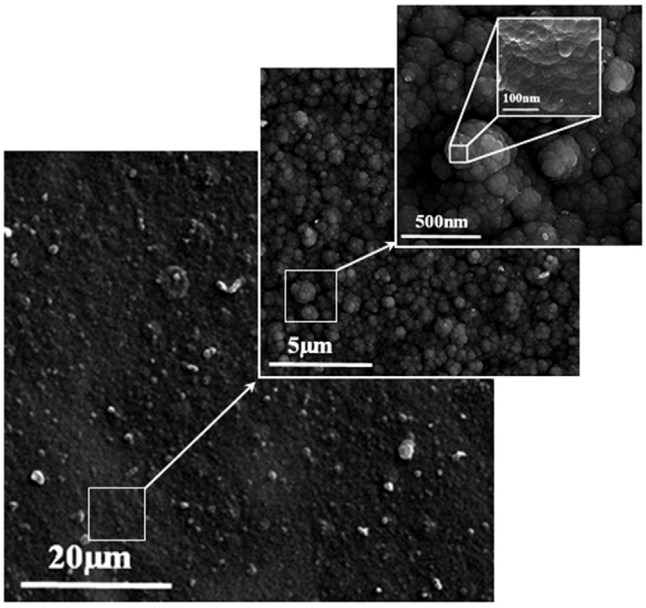

Fig. 14. Surface morphology of AZ31 Mg alloy coated with Ppy in the optimum condition.

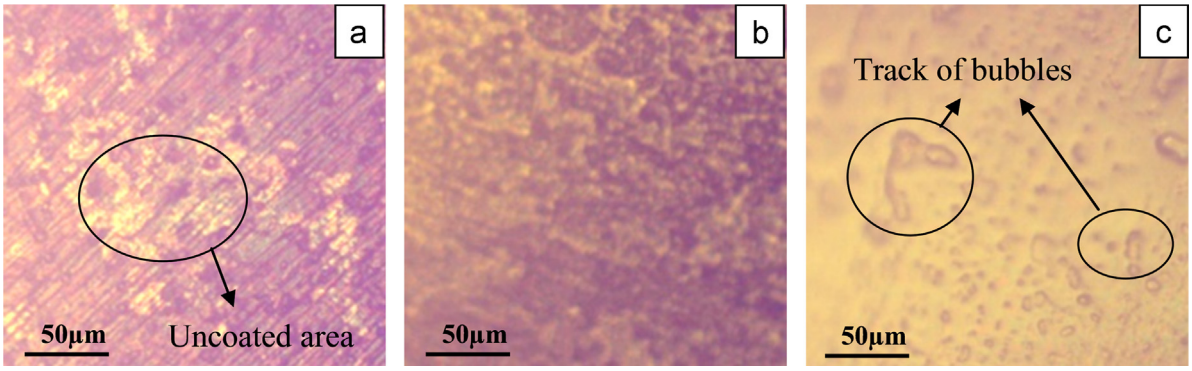

Fig. 12. OM images of Ppy coatings surfaces electrosynthesizedfor different cycles of. (a) 5, (b) 10 and (c) 20.

3.4. Protective performance of the coating electropolymerized in the optimum condition

Fig. 14 shows morphology of the coating prepared in 0.5 M sodium salicylate solution containing 0.25 M Py using cyclic voltammetry method in the potential range of 0–1200 mV at the scan rate of 20 mV/s for 10 cycles.

The SEM image demonstrated typical cauliflower morphology of Ppy grains with a diameter ranging from 20 nm to 60 nm.

The Nyquist plots of AZ31 Mg coated by Ppy synthesized in the optimal condition and those of the bare substrate are compared in Fig. 15. For both samples, the spectra were characterized with a capacitive loop at high frequencies and an inductive loop in low frequency region. Generally, the capacitive loop in the high and medium frequency region reflects the information of resistance capacitance relaxation process, which may be related to the charge transfer resistance R_{ct} and the electric double layer capacity C_{dl}.

The capacitive loop represents the charge transfer resistance, and the inductive loop may be linked to the formation of unstable Mg^+ ions in the Mg corrosion process [32]. The inductive loop is usually reported as a sign of active dissolution [33,34]. This effect can be explained by the presence of adsorbed species such as $Mg(OH)^+_{ads}$, $Mg(OH)_{2ads}$ and Mg^+_{ads}, and the absence of an inductive loop or any scattered data points in the low frequency region is the indication for better corrosion resistance [34,35]. An equivalent electrical circuit proposed to analyze the experimental data is shown in Fig. 16. Analysis of the experimental data has made by best fitting to the corresponding equivalent circuit using Zview software v.2.7, and the fitted EIS results of the samples are listed in Table 1. CPE expresses the double layer constant phase element; R_{ct} is the charge transfer resistance; n varies between 0 and 1 introduced to account for the deviation from the ideal capacitive behavior due to surface inhomogeneties, roughness factors and adsorption effects [36]. R_s is the solution resistance between the reference and working electrodes. Its value depends on the conductivity of the test medium and the geometry of the cell and has nothing to do with the electrode process [37]. R_L and L are related to the inductive loops in the EIS spectra. According to the figure, the charge transfer resistance of Mg coated by Ppy in the optimum condition enhances significantly from 387.1 to 5736 Ω cm^2.

Fig. 17 demonstrates the potentiodynamic polarization curves of the samples after 1 h of immersion in 3.5% NaCl solution. The amounts of corrosion current density and corrosion potential of the samples are listed in Table 1. The corrosion current, i_{corr}, was obtained from a Tafel plot by extrapolating the linear portion of the curve to E_{corr}. The superior corrosion resistance of Mg coated by Ppy under the optimum condition was clearly observed from a significant increase in charge transfer resistance and a noticeable drop in corrosion current density. As can be seen from the polarization

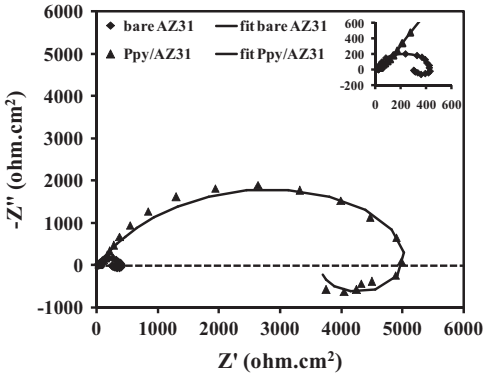

Fig. 15. Nyquist plots of AZ31 Mg coated by Ppy in optimal condition compared to the bare one.

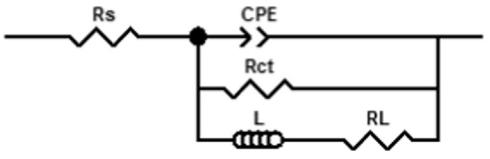

Fig. 16. Equivalent electrical circuits employed to analyze the data.

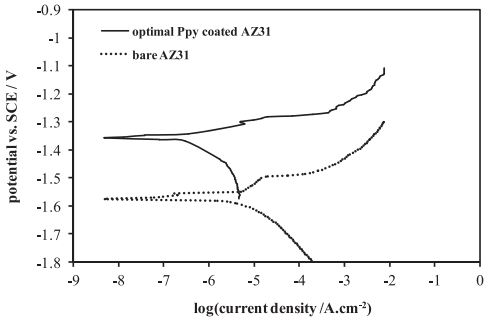

Fig. 17. Potentiodynamic polarization curves of AZ31 Mg coated by Ppy in optimal condition compared to the bare one.

Table 1
Calculated EIS parameters from equivalent circuit.

	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	CPE		R_L (Ω cm^2)	L (H)	E_{corr} (V)	i_{corr} (μA cm^{-2})
			P (μF cm^{-2})	n				
Bare AZ31	32.53	387.1	7.9	0.87	630	96.54	-1.48	5.7
Ppy/AZ31	33.49	5736	5.8	0.71	9978	2226	-1.36	0.12

curves, application of the Ppy coating on AZ37 Mg led to a 200 mV shift in the corrosion potential towards more positive potentials.

4. Conclusion

1. Ppy coating was successfully electropolymerized on AZ31 Mg alloy from aqueous sodium salicylate solution containing py monomer using cyclic voltammetry method.
2. In addition to an improvement in the adhesion quality of the synthesized Ppy coating on the Mg surface, the passivation pretreatment resulting from sodium salicylate solution could increase the corrosion resistance.
3. A uniform Ppy coating with the best adhesion and corrosion protection was provided from the electropolymerization of py in 0.5 M sodium salicylate containing 0.25 M Py using cyclic voltammetry method in the swiping potential of 0–1200 mV at 20 mV/s scan rate for 10 cycles.
4. According to the surface analysis and electrochemical data, an increase in the electropolymerization cycle over 10 had a negative effect on the Ppy coating performance.
5. The SEM image of the Ppy coated AZ31 Mg alloy demonstrated cauliflower morphology of Ppy grains with a diameter ranging from 20 nm to 60 nm.

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